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13. ABSTRACT *(Maximum 200 words)*

Electrostatic propulsion using C_{60} as the propellant has the potential to efficiently produce specific impulses in the range from 1000 to 3000 sec, and is therefore attractive for orbit transfer and station keeping missions. However, the viability of this concept depends on properties of the C_{60} molecule such as the ionization cross section, thermal stability, and resistance to fragmentation in a plasma environment. When this research began, insufficient information about these new materials was available. The objective of this program has been to determine properties of fullerenes relevant for electrostatic propulsion, to demonstrate ion extraction from a discharge, and to assess the implications for fullerene ion thrusters. The experiments we have undertaken fall into several distinct categories: time-of-flight mass spectrometry, electron energy loss spectroscopy, Fourier transform infrared spectroscopy, thermal stability, polarizability, and discharge chamber experiments.

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FINAL TECHNICAL REPORT

RESEARCH ON ELECTROSTATIC PROPULSION USING C_{60} MOLECULES

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Research Objectives

Electrostatic propulsion using C_{60} as the propellant has the potential to efficiently produce specific impulses in the range from 1000 to 3000 sec, and is therefore attractive for orbit transfer and station keeping missions. However, the viability of this concept depends on properties of the C_{60} molecule such as the ionization cross section, thermal stability, and resistance to fragmentation in a plasma environment. When this research began, insufficient information about these new materials was available. The objective of this program has been to determine properties of fullerenes relevant for electrostatic propulsion, to demonstrate ion extraction from a discharge, and to assess the implications for fullerene ion thrusters. The experiments we have undertaken fall into several distinct categories: time-of-flight mass spectrometry, electron energy loss spectroscopy, Fourier transform infrared spectroscopy, thermal stability, polarizability, and discharge chamber experiments. Below, we outline the major findings of these studies, and discuss their significance in the development of fullerene ion propulsion.

Experiments Performed and Results of Research

Time-Of-Flight Mass Spectrometry

One of the most important properties of a propellant for electrostatic propulsion is its ionization cross section as a function of electron energy. We have measured the energy-dependent ionization efficiency for production both of C_{60}^{+} and C_{60}^{++} using a crossed electron beam-molecular beam geometry to create ions which are analyzed in a time-of-flight mass spectrometer (Figure 1). These data have enabled us to identify an appearance potential of 7.8 ± 0.2 eV for C_{60}^{+}. When normalized to the absolute measurement of Sai Baba (1994), these measurements yield ionization cross section values in very good agreement with other studies carried out at the same time as our work (Scheier et al., 1993; Lezius et al, 1993).

One of the more significant findings of this study is the second ionization potential of C_{60}. It is evident that the ionization potential via electron impact, 16.4 ± 0.03 eV is significantly lower than the value of 19.0 ± 0.03 eV measured by photoionization in other studies.

In addition, we conducted an exhaustive study of fullerene cracking patterns as a function of electron energy. Multiple ions of C_{60} were observed (through C_{60}^{4+}). Only even numbered fragments were observed (C_{58}, C_{56}, C_{54}, etc...), but only at electron energies above 70 eV (Figure 2). Ion engines typically operate with electrons at energies between 20 and 30 eV, such that only the tail end of the electron energy distribution would result in fragmentation. Double and triple fullerene ions were evident in the spectra. Spectra extending to lower mass-to-charge ratios frequently showed quadruple fullerene ions as well.

Electron Energy Loss Studies

Another focus of this project has been to conduct studies of the electron energy loss spectra (EELS) of gas phase C_{60} and C_{70} in the energy range of interest for electric propulsion. These data can be used to determine total excitation cross section when integrated over all scattering angles. Electrons ranging in energy between 8 and 100 eV were scattered from a molecular beam of fullerenes. Scattered electrons were collected at scattering angles between 0 and 90 degrees. The observed broad spectral features in the resulting electron energy loss spectra were then assigned to overlapping electronic transitions. Pure vibrational excitations were also observed.

Energy loss peaks found in this investigation of gas phase fullerenes corresponded closely to those observed previously in both solid and solution phases of fullerenes, although some previously reported features were not observed here. Peaks were observed at 2.35, 3.72, 4.82, 6.1, and 7.5 eV. The spectra for C_{60} and C_{70} were quite similar, but not identical. The photoabsorption cross section derived from the 100 eV, 0 degree spectrum agrees within 10% with those published previously, except in the 5 to 7 eV region where the values obtained in this study are considerably smaller. In addition, studies of the fluorescence spectrum of C_{60} and C_{70} under electron impact excitation were performed,

showing no luminescence features from C_{60} or C_{70} in the region spanning from 180 to 750 nm. However, fluorescence was detected from two adducts of C_{60} ($C_{60}OH$ and $C_{60}H$). In these adducts, simultaneous ionization and excitation takes place under electron impact and the excited ionized species ($C_{60}^{+}OH^*$ and $C_{60}^{+}H^*$) decay radiatively. Electron energies of 20, 30, and 103 eV were used.

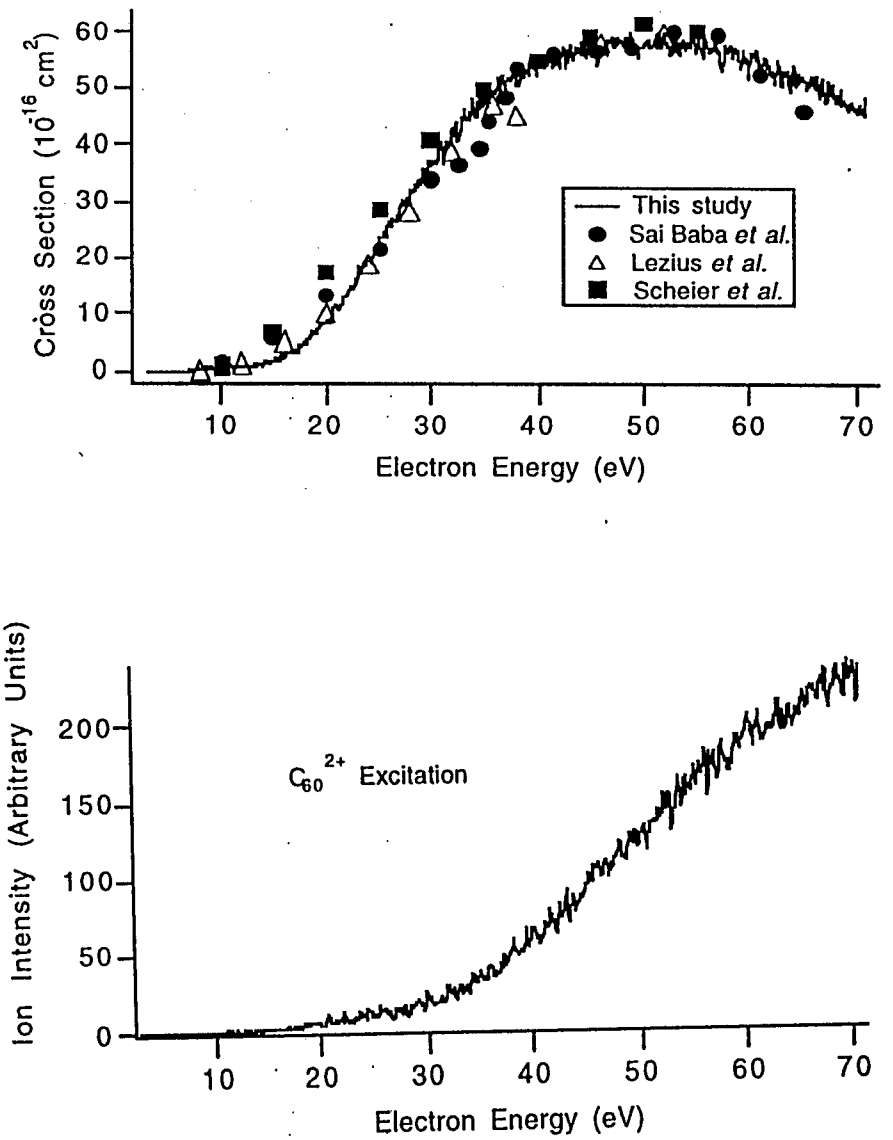

Figure 1: Ionization function curve for formation of C_{60}^{+} (top) and C_{60}^{++} (bottom).

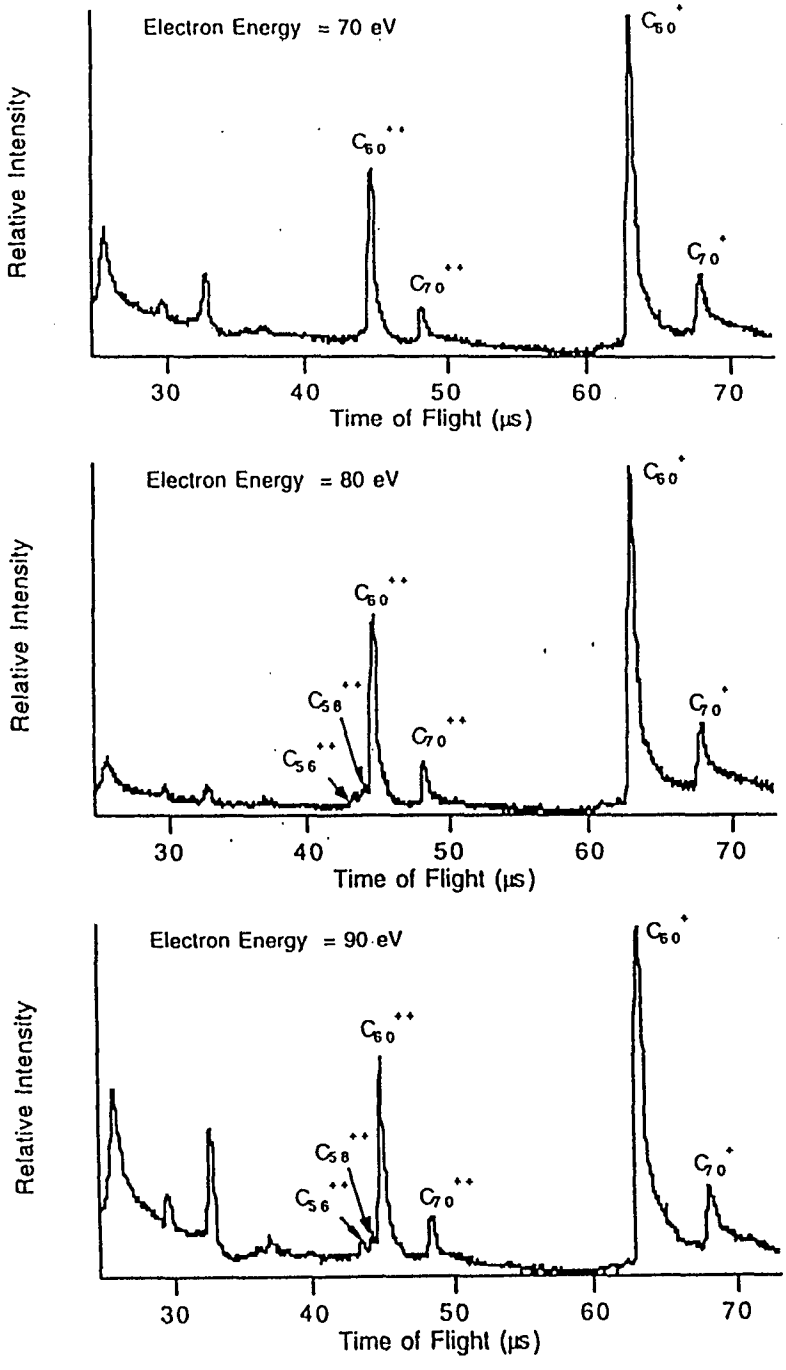

Figure 2: Cracking patterns for mixed fullerenes for electron impact energies from 70 to 90 eV.

Thermal Stability

Since fullerenes became available in macroscopic quantities in 1991, there have been numerous studies of the oxidative behavior of C_{60} and C_{70}. However, very few investigations of the thermal stability of fullerenes have been reported, particularly at temperatures above 973 K. Since most fullerene thruster concepts employ a heated effusive cell to supply the fullerene vapor, the thermal stability of fullerenes at elevated temperatures over long times has to be addressed.

To determine the thermal stability of fullerene mix, we filled quartz ampoules with approximately 10 mg of fullerene powder each. We prepared sets of 5 ampoules at a time with fullerene extract containing C_{60} and C_{70} in a ratio of approximately 85% to 15%. The fullerene mix was Soxhlet extracted with toluene from soot. Pure C_{60} and C_{70} were used as standards for compositional analysis. The fullerene-containing ampoules were placed under vacuum in the mid 10^{-6} Torr range and heated to temperatures between 473 K and 523 K to eliminate solvent and hydrocarbon impurities. The ampoules were then vacuum sealed and placed in a tube furnace for durations of 5 minutes to 6 hours. We prepared sets of samples heated to 873 K, 973 K. 1073 K, 1123 K, 1148 K, 1173 K, and 1273 K. The contents of the ampoules were analyzed for fullerene content. By curve fitting the fullerene decay curves to an exponential function, we obtained decay constants, k(T). An Arrhenius plot of our measured k(T) is shown in Figure 3. The Arrhenius activation energy was found to be 265.6 ± 8.9 kJ/mol. The pre-exponential factor was $1.24 \times 10^{9} s^{-1}$. The thermal disintegration we observed for C_{60} occurs at significantly lower temperatures than those predicted by molecular dynamics simulations. We believe that another mechanism for fullerene disintegration, possibly involving ring-rearrangement in the fullerene cage, is responsible.

The relatively rapid thermal decomposition of C60 we have found indicates several things. First of all, filament cathode discharges are likely to be a problem, since the hot filament will rapidly decompose any fullerene contacting it, likely leading to filament failure. Also, if effusive sources are used, they must be kept at a relatively low temperature. This in turn will keep the fullerene vapor pressure low, and therefore the mass flow rate from the source. For example, a source temperature of 1000 K will result in a decomposition time of 1.5 hours; at this temperature, the vapor pressure is less than 1 Torr.

Discharge Chamber Experiments

A discharge chamber was constructed and used to examine some characteristics of fullerene plasmas and to investigate C_{60}^{+} ion extraction under conditions similar to those expected for an electrostatic thruster operating on C_{60}.

DC Discharge

A filament cathode discharge chamber was operated for a maximum duration of 45 minutes with C_{60} at a minimum discharge voltage of 22 V. Difficulties were encountered with severe erosion of the tungsten filament cathode. In addition, rapid heating of the mixed fullerene sample in the effusive cell resulted in decomposition of the fullerene at

temperatures above 1073 K. Vacuum levels were in the 10^{-5} Torr range during this heating.

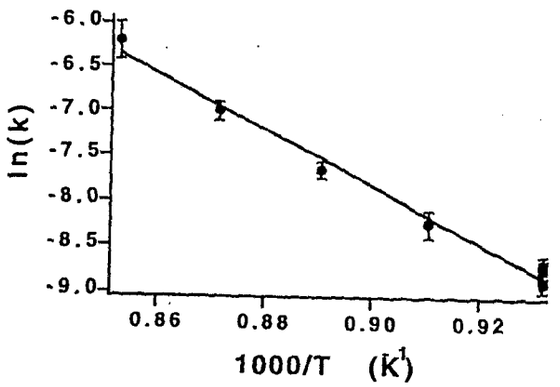

Figure 3: Arrhenius plot of the measured rate constant (s^{-1}) for thermal disintegration of a C_{60}/C_{70} mixture.

RF Discharge

To avoid the presence of high temperature metal surfaces, we constructed an RF discharge chamber (Figure 4). We used an Eni Power Systems 13.56 Mhz RF power generator and impedance matching circuit to reduce reflective RF losses from the engine. The discharge chamber consists of a 7.0 cm high, 7.0 cm diameter cylindrical quartz vessel with an extraction grid system and an oven containing the fullerene propellant flanged to opposite ends. An RF coil wrapped around the outside of the quartz vessel induces an azimuthal electric AC field inside the chamber. The fullerene plasma is maintained inductively, eliminating the need for hot electrode surfaces inside the discharge chamber. Ignition of the discharge may be obtained by RF breakdown or with the aid of electrons attracted from the neutralizer filament into the discharge chamber by temporarily applying a positive voltage to the screen grid. The RF field further accelerates the electrons inside the discharge chamber, leading to breakdown. A small orifice in the side of the effusive cell faces a Quartz Crystal Microbalance (QCM) which gave real-time flow rate measurements. Beam diagnostics included the use of an ExB mass spectrometer which displays peaks of all of the species present in the ion beam.

A xenon/fullerene plasma was successfully generated in the thruster. The maximum extractable beam current was approximately 45 mA., and the production cost for a pure xenon plasma was 1400 eV/ion. We believe this may be reduced by a factor of two with the use of higher open-area-fraction grids. (The lowest eV/ion cost of an RF thruster of this configuration is approximately 600 eV/ion achieved by the German RIT 4 thruster.)

The experiments using the C_{60} RF plasma discharge resulted in some interesting findings. When a plasma discharge was initiated with xenon, and C_{60} vapor was added to the plasma, a decrease in total beam current resulted, even though fullerene ions could

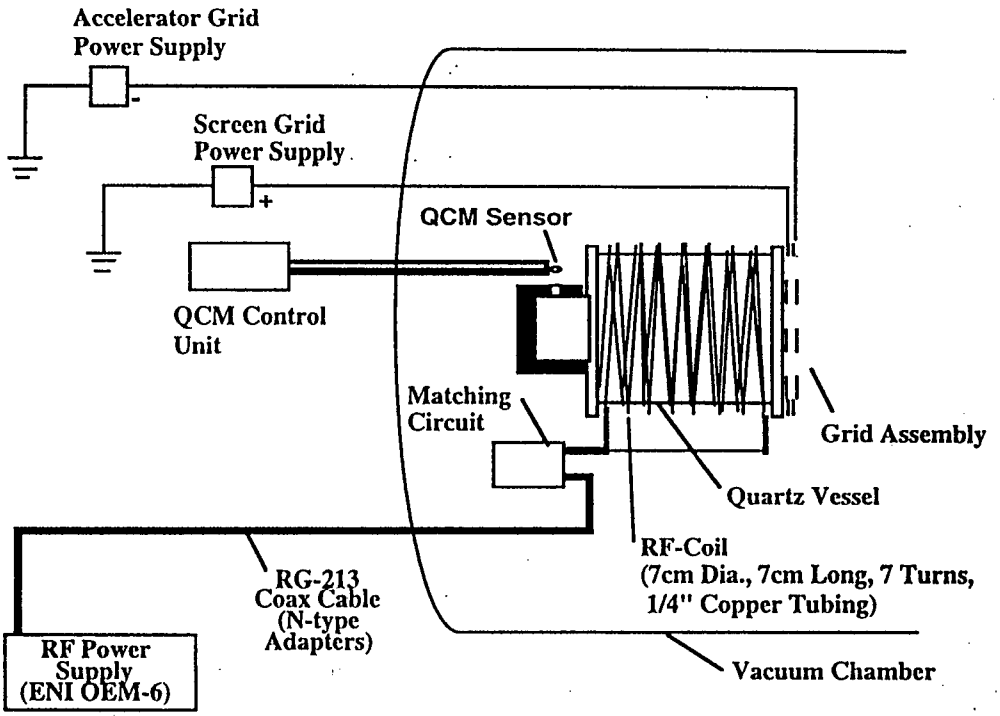

Figure 4: Schematic diagram of fullerene RF thruster.

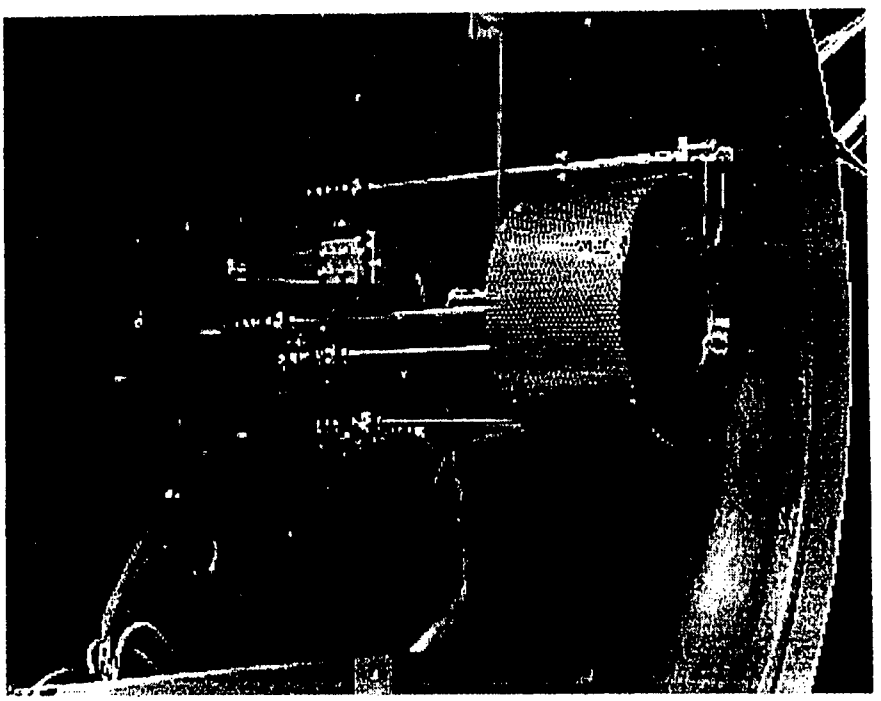

Figure 5: Fullerene RF ion thruster mounted in the vacuum facility

extracted from the discharge chamber. We also found that we were unable to initiate a pure fullerene RF discharge. The cause of both of these phenomena can be found in the electron attachment cross section of C_{60}; this cross section is very large for electron energies up to 14 eV. We estimate that it would be necessary to maintain a Maxwellian electron temperature of 10 eV or greater for the positive fullerene ion production rate to exceed that of the negative ion production rate.

Dissocation of C_{60} in the Discharge

One problem encountered in fullerene ion engines has been dissociation of the propellant. Previously this was attributed to thermal decomposition due to operation of the ion engine at temperatures greater than 1070 K. However, during tests conducted at temperatures lower than 1070 K fullerene fragmentation was still observed. This prompted an investigation to determine if the dissociation was still due to thermal effects or due to collisional processes in the discharge chamber. For this purpose, an ExB probe designed to discriminate between singly ionized C_{60} and C_{58} was built. This probe was used to determine the composition of positively charged particles extracted from a filament cathode ion engine. During these tests the ion engine was operated at temperatures below 910 K and fullerene fragmentation was not observed in the vaporizer used to supply C60 to the discharge chamber. This result suggests that thermal dissociation is not a problem in the ion engine. However, ExB data obtained during these tests show that between 70 to 85% of the charged particles extracted from the ion engine are fullerene fragment ions. In addition, dissociated fullerene residue was found in the discharge chamber after running the engine. Typically this residue accounted for up to 2/3 of the C_{60} mass supplied to the discharge chamber during an experiment. Because of these results the dissociation is attributed to collisional processes occuring in the discharge chamber.

Fullerene dissociation must be controlled for use of C60 as a propellant. Fragmented fullerenes coat the surfaces of ion engine electrical insulators with a conducting carbon film; they can also form flakes which can short the beam extraction electrodes. This causes arcing and results in poor ion engine performance. The testing described above was conducted at discharge voltages of ~40 V. Operation at lower voltage may result in less dissociation; however, because C_{60} forms negative ions, it is unlikely that fragmentation rates can be reduced enough keep ion engine performance from degrading significantly after a few hours of operation. Negative ions are trapped in the discharge chamber and must be nuetralized or positively ionized before they can be extracted from the discharge chamber. While trapped in the discharge chamber these ions will undergo energetic collisions and are likely to fragment.

Fullerene Contamination and Adsorbates

We conducted a study of fullerene contaminants and adsorbates using Fourier Transform Infrared (FTIR) spectroscopy. For solid fullerene samples, Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy is a simple and effective analytical tool which we have found to be particularly useful for analyzing C_{60} purity, reaction, products, and yields in crude fullerene soot extracts. The DRIFT technique is very sensitive to impurities and weak spectral features.

Examination of C_{60} dissolved in various solvents, as well as the solid fullerene samples studied by DRIFT spectroscopy, reveals that features in the 2350, 2330, and 1540 cm^{-1} region of the spectrum are intrinsic to C_{60} and do not result from CO_2 or oxygen contamination. By increasing the CO_2 content of solid C_{60}, we are able to observe new features at 2377, 2330, and 2316 cm^{-1}, different from the vibrational modes at 2328 and 2349 cm^{-1}. The peak observed at 1539 cm^{-1} in the solid vanishes when fullerene is placed in solution, but reappears when the sample is dried under nitrogen. We believe that the strength of this peak may be due to a Fermi resonance or a crystal field effect, both of which could be destroyed by solvent interactions in solution.

The results of this study relieve some concern over propellant contamination for fullerene ion thrusters. Though fullerenes do tenaciously hold solvents in the solid state, their affinity for gases such as CO_2 is not so great as one may have expected from infrared spectroscopic evidence. Infrared spectroscopy has provided a valuable tool for confirming that the cause of fullerene thermal disintegration investigated previously is not sample contamination.

Conclusions

The research conducted under this program has been an investigation of some fundamental properties of C_{60} relevant to fullerene ion thruster development. We have found from time-of-flight mass spectroscopy that fragmentation of C_{60} by electron impact is not significant for energies below 70 eV. Nevertheless, the discharge chamber experiments show substantial fragmentation of the extracted charged species when operated at 40 V. We postulate that this may be due to negative ions which form readily in the discharge and become trapped, eventually undergoing energetic collisions.

The thermal stability of fullerenes in solid form is also not as great as had originally been anticipated. As a result, conventional hollow cathode ion thrusters cannot operate with C_{60}. We examined the use of an RF fullerene thruster, but found that electron attachment cross sections for C_{60} remain large, up to 14 eV electron energies, requiring a high Maxwellian electron temperature in the discharge chamber.

Our results suggest that using C_{60} in a standard electrostatic thruster is unlikely to be successful, unless innovative approaches are taken to overcome the problems identified in the course of this research, which are essentially a) thermal stability, b) negative ion formation, and c) fragmentation in the discharge. Possible approaches to overcome some these problems might include extraction of negative ions rather than positive ones (requiring novel neutralization schemes), photoionization, and the use of cold cathodes.

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